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9, rue Gustave-Revilliod, CH-1227 Carouge (CH). KIR-  
BERG, Karl-Wilhelm; Hattsteiner Weg 7, 61267 Neu-  
Anspach (DE).

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(74) Agents: V. RAFFAY, Vincenz et al.; Geffckenstrasse 6,  
20249 Hamburg (DE).

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(71) Applicants: PONGS & ZAHN PLASTICS AG  
[DE/DE]; Albert-Einstein-Ring 10, 22761 Hamburg (DE).  
E.I. DU PONT DE NEMOURS AND COMPANY  
[US/US]; 1007 Market Street, Wilmington, DE 19898  
(US).

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(72) Inventors: EICKHOFF, Norbert; Reinthalerstrasse 20,  
28213 Bremen (DE). STELZER, Olaf; Grevesmühlener  
Strasse 37, 19057 Schwerin (DE). GREULICH, Stefan;

(54) Title: COMPOUND FOR A COMPOSITE BODY

(57) **Abstract:** The invention relates to a compound for the production of a composite body, comprising: a hard component (a) of a polyacetal, namely polyoxymethylene (POM) and a soft component (b) of one or more thermoplastic styrene elastomers (TPE), namely hydrogenated styrene block copolymer(s), which is moulded directly on to component (a). In the prior art the inadequate adhesion for some intended uses has manifested itself as a disadvantage of such a choice of materials for the components. The invention provides a remedy for this in that the styrene block copolymer(s) are poly-isoprene/butadiene polymer(s) (SEEPS) and/or poly-isoprene polymer(s) (SEPS) and/or poly-butadiene polymer(s) (SEBS), and in that the styrene block copolymer(s) are adhesion-modified, wherein styrene/butadiene copolymer (SBS) and/or ethylene/vinyl acetate copolymer (EVA) and/or olefinic materials, such as PE, PP, polystyrene (PS) are added as modifiers of the styrene block copolymer(s). One or more of the following substances are additionally added as modifiers of the polyoxymethylene: styrene/butadiene copolymer (SBS); ethylene/vinyl acetate copolymer (EVA); hydrogenated styrene block copolymer based on a hydrogenated poly-isoprene/butadiene rubber (SEEPS); hydrogenated styrene block copolymer based on a hydrogenated poly-isoprene rubber (SEPS); hydrogenated styrene block copolymer based on a hydrogenated poly-butadiene rubber (SEBS); compound based on a hydrogenated styrene block copolymer which can be present as hydrogenated poly-isoprene/butadiene rubber or as hydrogenated poly-isoprene rubber (SEPS) or as hydrogenated poly-butadiene rubber (SEBS); olefinic substances, such as PE, PP; polystyrene (PS), ABS, PC, SAN, TPE-U. The composite body according to the invention has excellent adhesion and sealing properties and can therefore be employed for a large number of intended uses in motor vehicle construction etc.

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## COMPOUND FOR A COMPOSITE BODY

The invention relates to a compound according to the precharacterizing clause of the main claim, and to a composite body produced therefrom and a process for its production.

Such a compound or composite body and also its production process are described, for example, in WO 00/20204 and DE 198 45 235. These already known doctrines require the use of a relatively expensive 5 non-olefinic thermoplastic material, which requires expenditure during compounding, in the form of polyester-urethane elastomers, polyether-urethane elastomers, polyesters, polyamides, polycarbonates, polyacrylates etc. A supposedly significant improvement in the adhesion between POM and elastomers of the TPE-S type is said to be achieved by this means. This pairing of materials has also already been presented at various technical conferences, e.g. "Thermoplastic Elastomers" at SKZ Würzburg, May 1999 10 and June 2000, at which, however, the mechanical properties, the resistance and the bonding adhesion values according to the general state of knowledge were rated as too low for many cases of use. The multicomponent injection moulding process has also already been mentioned according to the previously known doctrine for the production of the composite body, and enjoys a constantly increasing demand since the properties of hard and soft materials in one composite body can be combined in one production step.

15 The combination of POM with TPE-S is of particular interest, since both materials are distinguished by a number of unique properties.

POM is known for:

- outstanding mechanical properties (high tensile strength, impact strength, rigidity, fatigue resistance)
- 20 - excellent resistance to moisture, motor fuel, lubricants, solvents, neutral chemicals
- excellent dimensional accuracy
- good electrical insulation properties
- creep resistance
- low friction
- 25 - broad operating temperature range.

Polyoxymethylene is employed in the car, domestic appliance, installation, machine construction, tool, electronics and consumer goods industry. The use for many moving parts, such as gear components, deflection pulleys, toothed wheels or adjusting levers, due to its good sliding friction properties, and the use for snap connections, due to its excellent rebound resilience, are to be emphasized in particular.

30 TPE is known for:

- widely variable hardness range (Shore A = 10 to Shore D = 60)
- low density
- good recovery properties
- outstanding mechanical properties
- 35 - high noise-damping
- good ageing properties and outstanding ozone properties

- wide flexibility range and comparatively small change in flexibility in a wide operating temperature range
- good resistance to acids and alkalis
- very good static friction.

5 Thermoplastic styrene elastomer is used in the same/similar branches of industry to polyoxymethylene (inter alia car sector, domestic appliance industry).

In particular, there is therefore a need for a combination of polyoxymethylene (POM) and one or more thermoplastic styrene elastomers (hydrogenated styrene block copolymer) in which the adhesion between the two components is greatly improved compared with the prior art and thus allow wide use of a 10 combination of POM/TPE-S in multicomponent injection moulding, without mechanical anchorings, such as e.g. expensive undercuts, being necessary.

15 The invention is therefore based on the object of improving the abovementioned compound for a composite body such that a large number of uses where the combination of the specific properties of these two materials is advantageous can be opened up with it, such as e.g. in the case of fixing clips with a moulded-on projecting seal, e.g. in vehicle construction, fixing elements with a damping function, e.g. for motor fuel lines, sliding switches with a non-slip touch surface, casings for door locks with a seal injection-moulded on, and general soft-touch surface on POM components with excellent haptic properties.

Surprisingly, this object is achieved by the compound characterized in claim 1.

20 The TPE-S in the compound according to this invention is thus based on a hydrogenated styrene block copolymer, which can be present as hydrogenated poly-isoprene/butadiene rubber (SEEPS) or as hydrogenated poly-isoprene rubber (SEPS) or as hydrogenated poly-butadiene rubber (SEBS) and comprises the following substances which lead to improvement in the adhesion to POM:

styrene/butadiene copolymer (SBS) and/or  
ethylene/vinyl acetate copolymer (EVA) and/or  
olefinic materials, such as PE, PP and/or  
25 polystyrene (PS), where the use of non-olefinic thermoplastics can welcome be omitted.

The modifications can be made to the compound solely or also in combination.

30 Although these modifications made in the TPE for promoting adhesion are generally known, an improved adhesion to POM is described nowhere, so that an effect so positive was not to be expected in respect of POM. Rather, it is to be regarded as surprising that this modification brings not only the improvement sought in the composite to styrenic thermoplastics, but also a very good adhesion to POM.

35 The POM involved according to this invention in the compound belongs to the group of generally known polyoxymethylenes, which are built up either from the homopolymer of formaldehyde or from the copolymer of formaldehyde or its cyclic oligomers and cyclic ethers, cyclic acetals and/or linear acetals, and generally has a melt index (MFR according to ISO 1133) of between 0.5 and 75 g/10 min.

Modified types of POM can advantageously also be used simultaneously for the compound, which is preferred, such as e.g. mixtures of POM with one or more of the following polymers:

## TPE-U

styrene/butadiene copolymer (SBS),

ethylene/vinyl acetate copolymer (EVA),

hydrogenated styrene block copolymer based on a hydrogenated poly-isoprene/butadiene rubber

5 (SEEPS),

hydrogenated styrene block copolymer based on a hydrogenated poly-isoprene rubber (SEPS),

hydrogenated styrene block copolymer based on a hydrogenated poly-butadiene rubber (SEBS),

compound based on a hydrogenated styrene block copolymer, which can be present as hydrogenated poly-isoprene/butadiene rubber or as hydrogenated poly-isoprene rubber (SEPS) or as 10 hydrogenated poly-butadiene rubber (SEBS),

olefinic materials, such as PE, PP,

polystyrene (PS),

ABS, PC, SAN.

By the choice of mixture components in the POM, the adhesion to the TPE-S can be further 15 optimized according to the composition thereof.

It should be clear that a compound for the preparation of the composite body according to the invention can also additionally comprise other typical additives, in addition to the modifiers mentioned, such as paraffinic plasticizer oil for rubber and additives/stabilizers (inter alia heat stabilizer, antioxidants, anti-ageing agents, ozone stabilizers, processing auxiliaries). The compound can furthermore also comprise 20 thermoplastic materials (inter alia olefins, styrenes) and fillers (inter alia calcium carbonate).

The composite body according to the invention is prepared by the multicomponent injection moulding process in a one-stage form (inter alia by the rotary, index plate, slider, transfer, co-injection/sandwich technique) or in a multi-stage form (insert technique) or by the multicomponent extrusion process (inter alia coextrusion).

25 As a rule, the hard material component (polyoxymethylene) is first injected into the injection mould. Thereafter, in the one-stage process the hard component is moved to the other injection unit by means of the rotary, index plate, slider or transfer technique and the soft component is injection-moulded on. The two-stage process in which the hard component which has been injection-moulded beforehand is inserted into the mould manually or by means of handling equipment and the soft component is then 30 injected-moulded on is another possibility. The reverse procedure, injection moulding the hard component on to the soft component, is also possible with the process just described. Bonding of polyoxymethylene with a thermoplastic styrene elastomer in the form of the co-injection/sandwich process is furthermore possible.

35 Various bonding adhesion experiments with products of the prior art in comparison with the composite bodies with a composition according to the invention are described in the following.

The compound comprises the following contents, based on 100 parts of rubber (styrene block copolymer):

Plasticizer oil	:	$\geq 10$ parts
Filler	:	$\geq 10$ parts
Thermoplastic	:	$\geq 10$ parts
Additives	:	$\geq 1$ part

5 The recipes are compounds according to the invention based on SEEPS, which differ by addition of components which have not yet been used for such a purpose:

1-50 wt.% SBS

1-50 wt.% EVA, such as e.g. EVA 28/05

or a combination of the two.

10 These series of experiments clearly show that the modifications according to the invention to TPE alone already lead to a clear improvement in the bonding to non-modified POM.

As regards the values stated in the table, which relate to the adhesion at the bonding point, it should be noted that these cannot be compared with data determined otherwise, since test methods recognized as standard do not yet exist. A quantitative comparison is therefore possible only internally.

15 The production process moreover has a great influence on the measurement values. This is also clear from the fact that the test specimens produced by the 2C process (table 1) give significantly higher values than the test specimens produced by insert moulding. These figures can thus be used only for internal qualitative comparison. The values stated in parentheses thus also cannot be compared directly with those without parentheses.

20 As is known, the bonding is as a rule improved if the two materials comprise a common or similar component. However, the problem often lies in an incompatibility of this component with one or other material, the hardness having a substantial influence on the adhesive bond. To enable the values to be compared, in the end it should be ensured that all the parameters coincide and are optimized.

25 It has been found that a small addition of SBS or the small addition of a TPE compound, such as e.g. Ponaflex S 660AD1, to POM brings a clear improvement to the bond and shows a good compatibility. It has furthermore been found that the addition of EVA to the TPE compound improves the adhesion by up to 20%. In another step, an attempt was made to compound adhesion-improving components both into the TPE and into the POM on a 2-screw extruder. These series of experiments resulted in the modifications listed in the table, as optimum compounds with good adhesion and without a noticeable limitation in the 30 typical properties.

Various experimental bonding adhesion experiments with a TPE, namely SEPS (TPE 1), and POM homopolymer with an MFI = 15 (POM-1) in any manner have thus lead to unsatisfactory results; no adhesion at all was achieved between these substances (see table 1).

35 The same inadequate results were found with the same POM with SEBS (TPE 4) (Shore A hardness = 35 to 45) (see table 1).

It was furthermore attempted to bond SEPS (TPE-1) to POM copolymer with an MFI = 9 (POM-5). Here also, no adhesion was again observed, regardless of whether the one- or two-stage multicomponent injection moulding process was used (see table 1).

A lack of adhesion in the one-stage multicomponent injection moulding process was likewise 5 observed when the SEPS of the experiment mentioned last was replaced by SEBS. Only when the more involved two-stage multicomponent injection moulding process was employed here was some adhesion with a tear strength value of 0.33 N/mm<sup>2</sup> to be found.

Surprisingly, it was then found that if adhesion-modified TPEs are employed, an outstanding 10 bonding adhesion to various POMs can be achieved. If these are also adhesion-modified, which is not absolutely essential, however, particularly good results are achieved, as the values listed in this context in table 1 and the combination of substances stated underneath the table show.

This test bar was produced by filling the cavity for the shoulders of the tensile test bar with the 15 harder POM material in a first step. The temperature of the melt is typically 215°C (205°C for the copolymer). After the melt has solidified, the mould is opened and rotated, and after closing, in the second step the soft TPE-S material, which has a material temperature of 210°C, is injected in. After solidification of this melt, the composite body can be removed from the mould.

The mould temperature in this experiment is 40°C, but can be varied in order to influence the dimensional accuracy and the ejectability of the parts. All the other process parameters, such as injection 20 pressure, holding pressure, injection speed and holding pressure time, can also be optimized according to the material combination. If the adhesion is adequate, a 2-component tensile test bar which has the material sequence of hard-soft-hard results. This is tested for tensile strength in a standard test machine. The force F (in N) or tension (in MPa) measured is a measure of the adhesion between the two materials.

In the 2-stage process the hard component is first injection-moulded. This is inserted into the mould in the cold state in a second step. The soft component is then injection-moulded on to the cold 25 inserted part.

If the adhesion between the components is not high enough, the multicomponent part cannot be removed from the mould without being destroyed. In this case, "no adhesion" is stated in the table.

TABLE 1

	TPE-1	TPE-2	TPE-3	TPE-4
POM-1	no adhesion	1.4 (0.91)	- (0.24)	no adhesion
POM-2	no adhesion	1.5 (0.91)	(0.60)	-
POM-3	no adhesion	1.5 (0.91)	(0.71)	(0.44)
POM-4	no adhesion	1.2 ( )	(0.90)	
POM-5	no adhesion	- (0.95)		no adhesion (0.33)
POM-6		1.5 (0.97)	- (0.76)	
POM-7		0.8 (0.80)	- (0.78)	

Table 1: Results for bonding adhesion [N/mm<sup>2</sup>] of various hard/soft combinations of POM and TPE-S determined on 2-component tensile test bars produced by one-stage multicomponent injection moulding (values in parenthesis produced by two-stage multicomponent injection moulding, insert moulding).

5 POM-1: POM homopolymer with an MFI of 15; no modification

POM-2: POM homopolymer with an MFI = 12; modification with 10% partly aromatic polyester TPE-U of 4,4'-methyldiphenyl diisocyanate, 1,4-butanediol and polybutylene adipate (e.g. US 5,286,807 or US 4,804,716)

10 POM-3: POM homopolymer of MFI = 15; modification with 10% styrene/butadiene copolymer

POM-4: POM homopolymer of MFI = 15; 10% TPE-S compound (Ponaflex S 660 ADI)

POM-5: POM copolymer with an MFI = 9; no modification (product of Ticona Hostaform C9021 NC)

POM-6: POM homopolymer of MFI = 15; modification with 5% SEEPS and 5% SBS

15 POM-7: POM homopolymer of MFI = 15; modification with 10% ethylene/vinyl acetate (EVA 28/05)

POM-8: POM homopolymer with an MFI = 2.1; modification with 15% partly aromatic polyester TPE-U of 4,4'-methyldiphenyl diisocyanate, 1,4-butanediol and polybutylene adipate

POM-9: POM homopolymer with an MFI = 1.9; modification with 30% partly aromatic polyester TPE-U of 4,4'-methyldiphenyl diisocyanate, 1,4-butanediol and polybutylene adipate.

POM-10: POM homopolymer of MFI = 15; modification with 1% styrene/butadiene copolymer

POM-11: POM homopolymer of MFI = 15; modification with 1% ethylene/vinyl acetate (EVA

5 28/05)

POM-12: POM homopolymer of MFI = 15; modification with 10% SEEPS

POM-13: POM homopolymer of MFI = 15; 5% TPE-S compound (Ponaflex S 660 AD1) + 5% SEEPS

POM-14: POM homopolymer of MFI = 15; modification with 5% ethylene/vinyl acetate (EVA  
10 28/05) + 5% SEEPS

POM-15: POM homopolymer of MFI = 15; modification with 1% SEEPS

TPE-1: SEPS compound: no modification, Shore A = 60 (Ponaflex S 67660 B-LOH-G)

TPE-2: SEPS compound: modification with SBS Shore A = 50 (Ponaflex S 650 A)

TPE-3: SEPS compound: modification with EVA Shore A = 60 (Ponaflex S 660 AD1)

15 TPE-4: SEBS compound from Kraiburg TC4 HAZ Shore A = 35-45

A table 2 with various bonding experiments is furthermore also given. This table 2 shows by way of extract the results of a more comprehensive series of experiments. From these, the TPE types S 650 A (a), S 660 AD (b) and S 260 AD (c) proved to be particularly suitable. The other types either show no adequate adhesion, or do not fulfil the properties sought.

20

TABLE 2

Recipe	<i>S 660 AD1 natural</i>	<i>S 6(6)50 A natural</i>	<i>S 660AD2 natural</i>	<i>S 260 AD natural</i>
Recipe composition	TPE-S compound with 10% EVA as an adhesion modifier	TPE-S compound with 25% styrene block copolymer as an adhesion modifier	TPE-S compound with 20% EVA as an adhesion modifier	TPE-S compound with 20% EVA and 20% SBS as adhesion modifiers
Adhesive strength to POM formaldehyde homopolymer				
POM-1	0.24	0.8	0.56	0.70
POM-2	0.6	0.75	0.55	0.74
POM-8		0.8	0.61	0.75
POM-9		0.9	0.67	0.68
POM-10	0.44	0.85	0.60	0.67

POM-15	0.46	0.86	0.56	0.69
POM-11	0.37	0.79	0.59	0.68
POM-3	0.71	0.96	0.79	0.73
POM-12	0.68	0.86	0.65	0.80
POM-13	0.63	0.79	0.77	0.82
POM-14	0.71	0.86	0.77	0.88
POM-6	0.66	0.96	0.73	0.83

The following substances were investigated for modification of POM:

TPU	1-40 wt.%
Styrene block copolymer (SBS, SEBS, SEPS or SEEPS)	1-40 wt.%
EVA	1-40 wt.%
5 TPE compound (e.g. Ponaflex S 67960M)	1-40 wt.%
Hydrogenated styrene block copolymer	1-40 wt.%

## CLAIMS

1. Compound for a composite body, comprising:
  - a hard component (a) of a polyacetal, namely polyoxymethylene (POM) and
  - 5 a soft component (b) of one or more thermoplastic styrene elastomers (TPE), namely hydrogenated styrene block copolymer(s), which is moulded directly on to component (a), characterized in that the styrene block copolymer(s) are poly-isoprene/butadiene polymer(s) (SEEPS) and/or poly-isoprene polymer(s) (SEPS) and/or poly-butadiene polymer(s) (SEBS),
  - 10 and in that the styrene block copolymer(s) are adhesion-modified, wherein styrene/butadiene copolymer (SBS) and/or ethylene/vinyl acetate copolymer (EVA), olefinic materials, such as PE (polyethylene), PP (polypropylene), polystyrene (PS)
  - 15 are added as modifiers of the styrene block copolymer(s).
2. Compound according to claim 1, characterized in that one or more of the following substances are added as modifiers of the polyoxymethylene:
  - styrene/butadiene copolymer (SBS),
  - ethylene/vinyl acetate copolymer (EVA),
  - 20 hydrogenated styrene block copolymer based on a hydrogenated poly-isoprene/butadiene rubber (SEEPS),
  - hydrogenated styrene block copolymer based on a hydrogenated poly-isoprene rubber (SEPS),
  - 25 hydrogenated styrene block copolymer based on a hydrogenated poly-butadiene rubber (SEBS),
  - compound based on a hydrogenated styrene block copolymer which can be present as hydrogenated poly-isoprene/butadiene rubber (SEEPS) or as hydrogenated poly-isoprene rubber (SEPS) or as hydrogenated poly-butadiene rubber (SEBS),
  - olefinic substances, such as PE, PP,
  - 30 polystyrene (PS), ABS, PC, SAN, TPE-U.
3. Compound according to claim 2, characterized in that the POM is built up from a formaldehyde homopolymer or formaldehyde copolymer or its cyclic oligomers and cyclic ethers, cyclic acetals and/or linear acetals.
4. Compound according to claim 3, characterized in that the POM has a melt index (MFR according to ISO 1133) of between 0.5 and 75 g/10 min.

5. Compound according to one or more of the preceding claims, characterized in that the modifiers of the styrene block copolymer(s) or of the polyoxymethylene are added in a weight range from 5 to 25 wt.%, based on the TPE or POM.
6. Compound according to one or more of the preceding claims 1 to 5, characterized by a better bonding adhesion in one-stage multicomponent injection moulding compared with two-stage multicomponent injection moulding by insert moulding.
7. Composite body produced from a compound according to one or more of the preceding claims 1 to 6.
8. Process for the production of the composite body according to one or more of the preceding claims, characterized by a multicomponent injection moulding process in a one-stage form, in particular by the rotary, index plate, slider, transfer or co-injection/sandwich technique, or in a multi-stage form by the insert process or by the multicomponent extrusion process, in particular coextrusion.
9. Use of the composite body according to one or more of the preceding claims, produced by the process according to claim 7, as fixing clips with a seal in vehicle construction, or as a fixing element with a damping function for motor fuel lines, as a sliding switch with a non-slip touch surface, as a housing for door locks with a seal injection-moulded on, or as lining for dashboards, side components and sun-roofs in motor vehicle construction.

## INTERNATIONAL SEARCH REPORT

National Application No

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**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 B32B25/08 C08J7/04 B29C45/16 C08L53/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 B32B C08J B29C C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 20204 A (HERBST RUDI ; SCHMIDT FRITZ (DE); TICONA GMBH (DE); KURZ KLAUS (DE)) 13 April 2000 (2000-04-13) cited in the application * das ganze Dokument, insbesondere Tabelle 1, Beispiele mit Komponente B1 * --- EP 0 863 184 A (KURARAY CO) 9 September 1998 (1998-09-09) * Tabelle 3, Beispiele 21,22 * page 8, line 17 -page 9, line 24; claims * Tabelle 7, Beispiele 64,65 * ---	1-9
X		1,3,6-9



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel: (+31-70) 340-2040, Tx. 31 651 epo nl,  
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## INTERNATIONAL SEARCH REPORT

Information on patent family members

1. International Application No

PCT/EP 02/00149

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